Potassium Organotrifluoroborates: New Partners in Palladium-Catalysed Cross-Coupling Reactions

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Keywords: Arenediazonium salts / Potassium organotrifluoroborates / Cross-coupling / Palladium / Biaryls / Styrenes

The preparation of various potassium organotrifluoroborates bearing either aryl, alkenyl, or alkynyl substituents is described. These stable salts are shown to be very efficient partners in palladium-catalysed cross-coupling reactions with arenediazonium salts, affording biaryl and styrene derivatives in high yields.

Introduction

Biaryl and styrene structural units are not only encountered in various natural products, but also in numerous technologies such as in the fields of molecular recognition, chiral ligands, nonlinear optics, liquid crystals, etc. Cross-coupling reactions between an aromatic electrophile and an organometallic species, catalysed by transition metals,[1] most often palladium or nickel, are methods of choice for gaining access to such structures.

Various organometallics have been employed in cross-coupling reactions since their discovery in the early 1970s,[2] the most frequently used being tin[3] (Stille coupling) and boron derivatives[4] (Suzuki coupling). All these cross-coupling reactions tolerate a broad range of functional groups because of the low nucleophilicity of the organometallic partner. Organoboranes have the advantage of being generally less toxic than organostannanes.

In the same way, different aromatic electrophiles can be used in cross-coupling reactions, the most routinely employed being the expensive aromatic iodides, bromides, and triflates. We,[5] and others,[6] have shown that stable arenediazonium tetrafluoroborates, derived from inexpensive aromatic amines,[7] are very efficient partners in cross-coupling reactions with organoboronic acids.

In our studies on cross-coupling reactions with arenediazonium salts, we sought more reactive organometallics. The use of nucleophilic organometallics such as magnesium or zinc compounds was out of the question since these reacted directly with the diazonium substituent, thereby leading to diazene derivatives.[8] Moreover, organostannanes gave only moderate results in coupling reactions with diazonium salts[9] other than in methylation reactions.[9][10] In our quest for alternative reagents, we recently found that potassium organotrifluoroborates show very high reactivity in palladium-catalysed cross-coupling reactions with arenediazonium salts.[11] We wish to report herein the preparation of a wide variety of potassium organotrifluoroborates and their use in reactions of this type.

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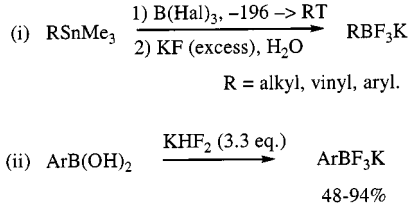
Preparation of Potassium Organotrifluoroborates

Organotrifluoroborate salts, or, more generally, compounds of formula $[R_nBF_{4-n}]^-$ ($n \leq 3$), have for a long time remained mere laboratory curiosities. Until very recently,[12] few compounds of this type had been prepared.

In 1940, Fowler and Kraus[13] described the preparation of tetraalkylammonium triphenylfluoroborates by reaction of the triphenylborane-ammonia complex with one equivalent of tetraalkylammonium fluoride, although no yields were specified. These salts, particularly those having potassium as the counterion, interested some authors in the early 1960s. Study of these systems was motivated by the formation of stable perfluoroalkylated boron derivatives. Trivalent boron compounds bearing a fluorine atom at an α or β position proved to be very unstable[14] (migration of the fluorine from carbon to boron), which is not the case with potassium organotrifluoroborates. The first such salt, potassium trifluoromethyltrifluoroborate, was prepared by Chambers et al.[15] from trifluoromethyltrimethylstannane (Scheme 1-i, R = CF_3).



Scheme 1. Formation of potassium organotrifluoroborates

Since then, other organotrifluoroborates have also been synthesized from the corresponding organostannanes[16] (Scheme 1-i). All these salts have been described as being very stable, even at elevated temperatures.

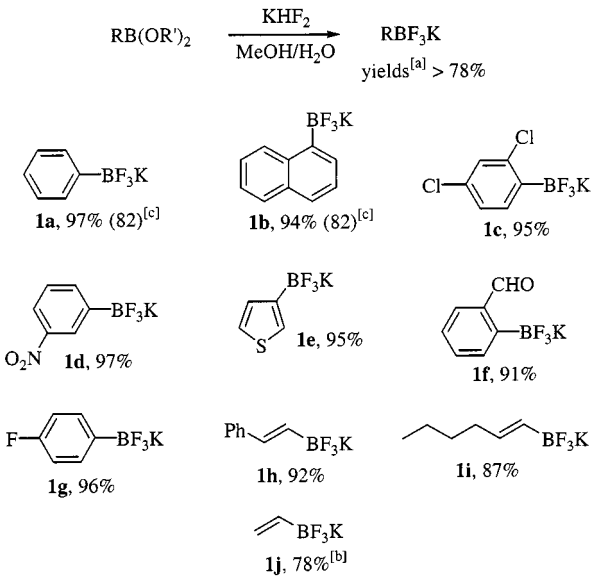
This approach was not satisfactory since it necessitated the intermediate preparation of organodihaloboranes. Following the preliminary results obtained by Thierig and Umland,[17] Vedejs et al.[12] showed that hydroxyl ligands of

  1434–193X/99/0808–1875 $ 17.50+.50/0

arylboronic acids could be displaced with potassium hydrogen difluoride (KHF_2), thereby leading to potassium aryltrifluoroborates (Scheme 1-ii).

Until now, the only utility of potassium organotrifluoroborates has been their ability to release organodifluoroboranes upon heating[16a] or treatment with chlorotrimethylsilane,[12][18] although very recently they have been used in the preparation of fluoroalkenes.[19]

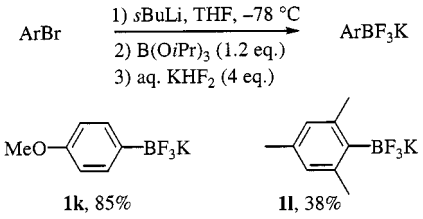
As described previously,[12] treatment of commercial arylboronic acids with aqueous KHF_2 resulted in the instantaneous deposition of a voluminous precipitate of the potassium aryltrifluoroborate. A slight modification of the original procedure[12] allowed us to obtain different potassium aryltrifluoroborates in almost quantitative yields and in analytically pure form (Scheme 2). After the addition of KHF_2, the solvents were removed in vacuo and the remaining solid was extracted with acetone. KHF_2 and other salts (KBF_4, KF, etc.) are insoluble in acetone, hence, on removal of the solvent from the extracts, very pure compounds were obtained. Where necessary, the product could be purified by reprecipitation from an acetone/diethyl ether mixture. This procedure proved to be very general and was used for the isolation and purification of all the described potassium organotrifluoroborates.



[a] Yields of analytically pure compounds. – [b] Prepared from 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane. – [c] In parenthesis, yields obtained in ref. [12].

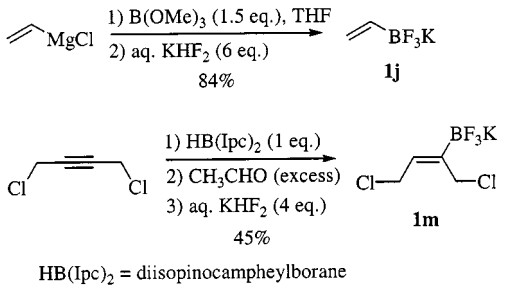
Scheme 2. Preparation of potassium organotrifluoroborates from organoboronic acids and esters

Potassium aryltrifluoroborates could also be prepared directly from aryl bromides by a sequence of classical bromine−lithium exchange, boronation, and in situ treatment with aqueous KHF_2 (Scheme 3), without having to isolate the intermediate boronic acid derivative. The lower yield obtained with 1-bromo-2,4,6-trimethylbenzene may reflect a hampering of the bromine−lithium exchange due to steric hindrance.



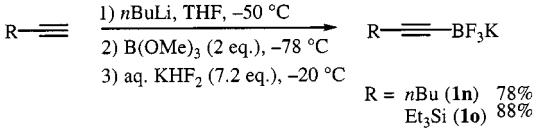
Scheme 3. In situ formation of potassium aryltrifluoroborates from aryl bromides

In the same way, treatment of the readily available alkenylboronic acids or esters[20a] with KHF_2 afforded the corresponding potassium alkenyltrifluoroborates in high yields (Scheme 2). Potassium hydrogen difluoride proved sufficiently reactive to cleave the boron−oxygen bonds in boronic esters. For example, potassium vinyltrifluoroborate **1j** was obtained in 78% yield from 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane, which was commercially available. Compound **1j** could be prepared more efficiently, on a large scale, by treatment of vinylmagnesium chloride with trimethoxyborane followed by in situ addition of KHF_2 (Scheme 4). Potassium alkenyltrifluoroborates could also be prepared directly from alkynes through hydroboration. For example, hydroboration of commercial 1,4-dichlorobut-2-yne with diisopinocampheylborane[20b,20c] followed by oxidation with acetaldehyde and in situ treatment with KHF_2 (Scheme 4) afforded **1m** in 45% yield.



Scheme 4. In situ formation of potassium alkenyltrifluoroborates

Finally, using the same methodology, it was possible to prepare potassium alkynyltrifluoroborates for the first time. These salts were obtained by deprotonation of alk-1-ynes, boronation, and in situ treatment with KHF_2 (Scheme 5). Interestingly, the triethylsilyl group was not removed by KHF_2 and compound **1o** was obtained in good yield. These compounds represent the first stable organoboron derivatives containing a C_{sp}−B bond, although the chemistry of alkynylborates has been well documented.[21] Generally, alkynylboranes are not stable and are readily hydrolysed in the presence of water or alcohols.[22]



Scheme 5. In situ formation of potassium alkynyltrifluoroborates

All of the described potassium organotrifluoroborates were found to be stable at room temperature for several years, except for **1m**, which had to be stored at 0°C. The products did not show any sensitivity towards oxygen or moisture, and are thus far more stable than the corresponding organoboronic acids or esters.[23] For example, vinylboronic acid is highly unstable and cannot be isolated;[24] its ester 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane is only slightly stable at −20°C under N_2, whereas **1j** may be kept at room temperature for several years without significant decomposition.

All of the described salts were found to be very soluble in DMSO, moderately soluble in acetone, ethanol, and methanol, and insoluble in ethereal solvents, chlorinated solvents, and hydrocarbons. Some of them also showed solubility in water, acetonitrile, and THF. The stability of the solid salts at elevated temperatures is reflected in their high melting points (Table 1).

The melting points of **1b** and **1j** are higher than those reported previously (205°C[12] and 225°C,[16a] respectively). The ^{11}B-NMR spectra each featured a reasonably well resolved 1:3:3:1 quadruplet, corresponding to the coupling of ^{11}B with the three fluorine atoms. This gave an indication of the substitution at the boron atom. In the ^{19}F-NMR spectra, 1:1:1:1 quadruplets were observed, as expected for the coupling of ^{19}F with ^{11}B of spin 3/2. In the ^{13}C-NMR spectra, the signal of the carbon α to the tetravalent boron was generally not observed.

Table 1. Some physical properties of potassium organotrifluoroborates

Entry	RBF_3K	m.p. (°C)	NMR[a] (δ, ppm) ^{11}B	^{19}F	$^2J_{B-F}$ (Hz)
1	**1a**	> 260	4.4	9.5 (br)	54
2	**1b**	221	4.8	11.7 (br)	53
3	**1c**	202	3.2	12.9	49
4	**1d**	≈ 260	3.6	6.1	50
5	**1e**	250–260		13.1 (br)	≈ 60
6	**1f**	224	4.1	14.4	53
7	**1g**	> 260	4.2	4.6 (br)	54
8	**1k**	> 260	4.4 (br)	8.0	54
9	**1l**	> 260	5.0	18.0 (br)	50
10	**1h**	> 260	3.8	10.4 (br)	46
11	**1i**	> 260	3.6 (br)	11.0 (br)	≈ 52
12	**1j**	241	3.4	7.1	56
13	**1m**	180-185[b]	3.0		51
14	**1n**	> 260	−1.8	17.7	38
15	**1o**	> 260	−2.4	16.7	37

[a] BF_3•Et_2O was used as internal standard. − [b] Decomposition.

In summary, we have succeeded in preparing various potassium organotrifluoroborates, most of them for the first time. As mentioned above, the products were found to be extremely stable compounds, both in the solid state and in solution. Moreover, their preparation and isolation has proved very straightforward compared to that of other organoboron derivatives, particularly organoboronic acids.

We then tested their reactivity in palladium-catalysed cross-coupling reactions with arenediazonium salts

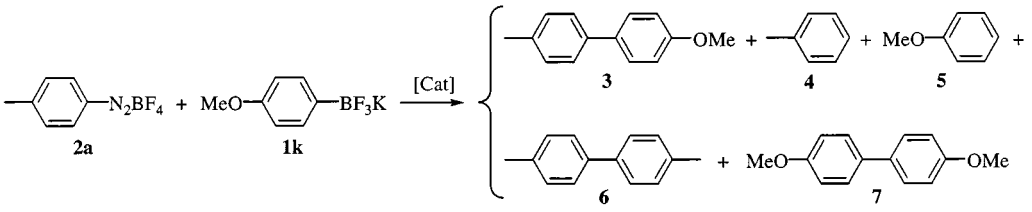
Cross-Coupling Reactions

Optimization

Optimization of the cross-coupling reaction was performed on two substrates: 4-methylbenzenediazonium tetrafluoroborate **2a** and potassium (4-methoxyphenyl)trifluoroborate **1k** (Scheme 6). At the end of the reactions, when evolution of N_2 had ceased, the crude mixtures were analysed by GC using an internal standard. In some reactions, besides the expected biaryl **3** some by-products were observed, arising mainly from reduction (**4** and **5**) and homocoupling (**6** and **7**) of these substrates.

We first studied the influence of the solvent on the course of the reaction using palladium acetate as catalyst (Table 2, entries 1−9). In polar solvents such as NMP (entry 1) or acetone (entry 2), yields were low. In the former, reduction product **4** was obtained as the major product, whereas in the latter, conversion was low due to rapid decomposition of the catalyst and significant quantities of the protodeboronation product were observed.

In protic solvents (entries 3−5), the results were more varied. In deionized water (entry 5), no reaction took place, which can be explained by the complete insolubility of **1k** in this medium. In alcoholic solvents, acceptable yields of biaryl **3** were obtained. Nevertheless, homobiaryls **6** and **7** were the major by-products in methanol, while reduction of the diazonium function occurred to a significant extent in ethanol. Moreover, coupling in methanol was extremely exothermic and took place within a reaction time of a few seconds. Decreasing the amount of catalyst or lowering the temperature did not improve the yields. It has been reported that in cross-coupling reactions with organostannanes[25] or organoboranes[26] the presence of oxygen favours homocoupling of the organometallic moiety. In the present case, oxygen had no effect on the extent of formation of **7**, but the reaction was slower.



Scheme 6. Optimisation of the cross-coupling reaction

Table 2. Optimization of the cross-coupling reaction[a]

Entry	Solvent	Catalyst (%)	Time (h)	Products obtained[b] (mmol) 3	4	5	6	7
1	NMP	$Pd(OAc)_2$	1.25	0.14	0.76	0.17	0.05	0.07
2	acetone	$Pd(OAc)_2$	0.05[c]	0.22	0.04	0.76	0.03	0.03
3	EtOH	$Pd(OAc)_2$	3	0.68	0.25	0.15	0.03	0.10
4	MeOH	$Pd(OAc)_2$	< 0.01	0.70	0.09	0.16	0.10	0.17
5	H_2O	$Pd(OAc)_2$	4[d]	0	0	0	0	0
6	THF	$Pd(OAc)_2$	3.5	0.63	0.30	0.48	0.04	0.04
7	dioxane	$Pd(OAc)_2$	4	0.86	0.02	0.27	0.01	0.05
8	dioxane/H_2O[e]	$Pd(OAc)_2$	0.05	0.54	0.42	0.18	0.02	0.12
9	dioxane/MeOH[e]	$Pd(OAc)_2$	1.75	0.82	0.08	0.43	0.05	0.06
10	dioxane	$Pd(dba)_2$	1	0.18	0.09	0.98	< 0.01	0.01
11	dioxane	Pd/C	51[f,g]	0.26	0.25	0.92	< 0.01	0.01
12	dioxane	**8**[i]	23[h]	0.31	0.02	0.04	0.06	0.04
13	MeOH	$PdCl_2$	2	0.47	0.16	0.26	0.19	0.17
14	MeOH	$Pd(dba)_2$	3	0.70	0.16	0.21	0.07	0.11
15	MeOH	$Pd(acac)_2$	0.25	0.73	0.04	0.08	0.11	0.13
16	MeOH	Pd/C	19[f]	0.06	0.05	0.32	< 0.01	< 0.01
17	MeOH	$Pd(OAc)_2$(bipy)	1.2	0.77	0.13	0.16	0.05	0.07
18	MeOH	**8**[i]	1	0.83	0.03	0.06	0.07	0.08

[a] Reactions were conducted with 1 mmol of **2a**, 1.2 equiv. of **1k** with 5 mol% of catalyst, in 4 ml of solvent at 20°C. Conversions, determined by the volume of N_2 evolved, were quantitative except when noted. – [b] Determined by GC using naphthalene as internal standard, taking into account the conversion. – [c] Conversion of 60%. – [d] No reaction. – [e] 10 Equiv. – [f] Reaction conducted at 40°C. – [g] Formation of 0.48 mmol of 4-fluorotoluene. – [h] Conversion of 45%. – [i] $Pd_2(\mu\text{-}OAc)_2(P(o\text{-tolyl})_3)_2$.

In ethereal solvents (entries 6 and 7), conversions were quantitative, with the best results being obtained in 1,4-dioxane (86%, entry 7). Addition of 10 equivalents of water to dioxane (entry 8) dramatically accelerated the reaction, but reduction product **4** was produced at the expense of **3**. Finally, addition of 10 equivalents of methanol (entry 8) shortened the reaction time without decreasing the yield.

Next, we tested the catalytic activity of various palladium complexes. In 1,4-dioxane, palladium acetate gave the best results. With $Pd(dba)_2$[27] or Pd/C (entries 10 and 11), which have been shown to be efficient catalysts in cross-coupling reactions with arylboronic acids,[5] yields were low and reduction of **1k** was almost quantitative. Moreover, the presence of phosphane ligands inhibited the coupling (entry 12).

The different catalysts were then evaluated in methanol. In the presence of homogeneous palladium catalysts free from phosphane ligands (entries 4, 13–15), significant amounts of homobiaryls were observed and yields of the desired coupling products did not exceed 70%. With a heterogeneous catalyst (Pd/C, entry 16), the coupling did not reach completion, even after 20 h at 40°C. The use of homogeneous palladium catalysts stabilized with diamine [$Pd(OAc)_2$(bipy),[28] entry 17] or phosphane ligands {$Pd_2(\mu\text{-}OAc)_2[P(o\text{-tolyl})_3]_2$ **8**,[29] entry 18} led to a decrease in the amount of homocoupling products. In particular, the palladacycle **8** proved to be very efficient, giving good yields of the expected biaryl **3**.

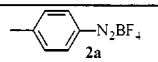
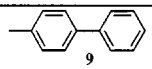
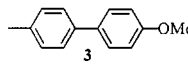
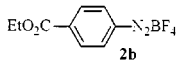
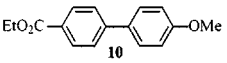
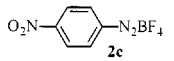
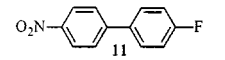
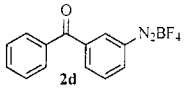
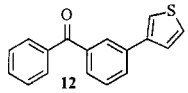
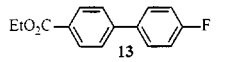
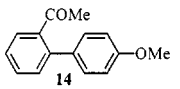
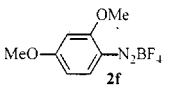
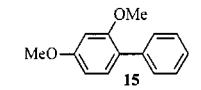
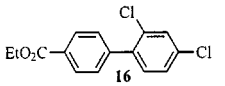
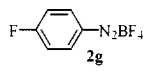
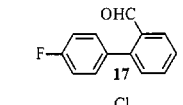
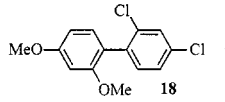
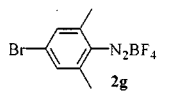
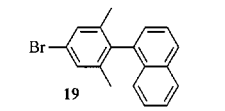
From this study, two favoured catalyst/solvent systems have emerged: $Pd(OAc)_2$/dioxane and **8**/methanol. With both these systems, good yields of the desired biaryl **3** are obtained, while formation of by-products is minimized.

Formation of Biaryls

The conditions established above were first applied to the formation of biaryls. Reaction of arenediazonium tetrafluoroborates[7] with potassium aryltrifluoroborates in the presence of 5 mol-% palladium acetate in 1,4-dioxane at 20°C (conditions A) afforded biaryls bearing diverse functionalities (Table 3, entries 1–2, 4–10). High yields were generally achieved, even when the diazonium salt was substituted at the *ortho* position (entries 8 and 9). Moreover, the reactivity of the aryltrifluoroborates was far superior to that of arylboronic acids,[5] and hence the isolated yields were higher (entries 4, 7, 9, and 10).

Table 3. Cross-coupling reactions of arenediazonium tetrafluoroborates with potassium aryltrifluoroborates[a]

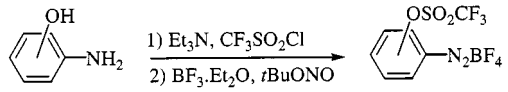
$$Ar\text{–}N_2BF_4 + Ar'\text{–}BF_3K \xrightarrow[A \text{ or } B]{\text{Condition}} Ar\text{–}Ar'$$

Entry	ArN_2BF_4	$Ar'BF_3K$	Time[b] (h)	Ar–Ar'	Yields[c]
1	 **2a**	**1a**	3.7 (A)	 **9**	(88) [87]
2	**2a**	**1k**	4 (A)	 **3**	(86)
3	**2a**	**1k**	1 (B)		(83)
4	 **2b**	**1k**	2 (A)	 **10**	93 [57]
5	 **2c**	**1g**	2.5 (A)	 **11**	92
6	 **2d**	**1e**	3 (A)	 **12**	86
7	**2b**	**1g**	2 (A)	 **13**	96 [49]
8	 **2e**	**1k**	1.7 (A)	 **14**	96
9	 **2f**	**1a**	6.5 (A)	 **15**	69 [32]
10	**2b**	**1c**	72[e] (A)	 **16**	(26) [5]
11	**2b**	**1c**	1.5 (B)		73
12	 **2g**	**1f**	4 (B)	 **17**	67
13	**2f**	**1c**	20[e] (B)	 **18**	traces[d]
14	 **2g**	**1b**	24 (A)	 **19**	21
15		**1b**	120 (B)		(10)

[a] See Experimental Section. – [b] In parenthesis, condition used: A: 1,4-dioxane/$Pd(OAc)_2$ 5%, B: methanol/**8** 5%. – [c] Isolated yields. Yields in parenthesis were GC yields and in square brackets yields obtained with the corresponding arylboronic acids. – [d] Detected by GC/MS, conversion of 10–20%. – [e] Reaction conducted at 40°C.

In the case of *ortho*-substituted aryltrifluoroborates, black palladium precipitated under conditions A, resulting in termination of the reaction (entry 10). However, with palladacycle **8** in methanol (conditions B), good yields of biaryls were obtained (entries 11 and 12). In a previous study, it was found that only traces of biaryls were produced using *ortho*-substituted arylboronic acids.[5b] An *ortho-ortho'* disubstitution was found to totally inhibit the reaction (entry 13). Nevertheless, using the very reactive naphthyltrifluoroborate **1b**, it was possible to obtain a tri-*ortho*-substituted biaryl in moderate yield (entry 14).

We then studied the chemoselectivity of the present cross-coupling reaction by treating arenediazonium salts bearing iodo, bromo, and triflate substituents. The latter were efficiently prepared in two steps starting from readily available aminophenols (Scheme 7). Treatment of these with triethylamine followed by addition of trifluoromethanesulfonyl chloride selectively afforded the *O*-protected amines. The use of triflic anhydride led to lower yields of aminotriflates.[30] The diazonium salts were then prepared in high yields under anhydrous diazotization conditions.[7c] In the case of the *meta* isomer, yields were low because chlorination of the aromatic ring also occurred and the diazonium salt was obtained as an inseparable mixture with this side-product.

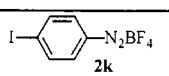
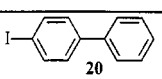
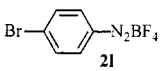
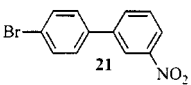
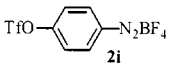
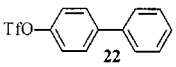


isomer *ortho* 77% **2h**
para 69% **2i**

Scheme 7. Formation of (trifluoromethanesulfonyloxy)benzenediazonium tetrafluoroborates from aminophenols

Conditions B were found to be most favourable for chemoselective coupling of the diazonium group (Table 4, entries 1−4). Once again, the yields of biaryls were superior to those obtained using the corresponding arylboronic acids.[5] In the coupling with diazonium salt **2k**, we also observed the presence of small amounts of by-products, namely 1,4-diiodobenzene and [1,1′;4′,1′′]terphenyl. The formation of such products could arise from a competitive insertion of palladium into the C−I bound.

Table 4. Chemoselectivity of the cross-coupling reaction[a]

Entry	ArN_2BF_4	$Ar'BF_3K$	Time[b] (h)	Ar–Ar'	Yield[c]
1	 **2k**	**1a**	22 (A)	 **20**	(32) [17]
2		**1a**	22 (B)		41
3	 **2l**	**1d**	30 (A)	 **21**	(53) [34]
4		**1d**	8 (B)		60
5	 **2i**	**1a**	1 (A)	 **22**	66

[a] See Experimental section. − [b] In parenthesis, condition used: A: 1,4-dioxane/$Pd(OAc)_2$ 5%, B: methanol/**8** 5%.− [c] Isolated yields. Yields in parenthesis were GC yields and in square brackets yields obtained with the corresponding arylboronic acids.

Formation of Styrenes and Derivatives

Styrene derivatives have often proved to be useful intermediates, particularly in the field of polymer-bound reagents and catalysts. Among the various available methods, transition metal-catalysed vinylation reactions have been most widely used for the preparation of such compounds.

Palladium-catalysed Heck reaction of aryl halides offers an easy and general access to substituted styrenes.[31] However, this reaction is sometimes limited because of further reaction to give stilbenes,[32] and by the harsh conditions of temperature and pressure required. For these reasons, many authors have developed organometallic vinylating agents for use in palladium-catalysed reactions, such as magnesium,[33] zinc,[34] silicon,[35] copper,[36] and germanium[37] vinyl derivatives. One of the most useful, vinyltributylstannane, was introduced by Stille et al.[38] Moreover, such couplings are generally limited to the rather expensive aryl iodides, bromides, and triflates. In the case of organoboron derivatives, cross-coupling reactions with vinylboronic esters are not selective.[39] A mixture of compounds deriving from both Suzuki and Heck coupling is invariably obtained.

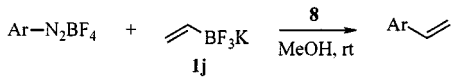
Arenediazonium salts, readily obtained from aromatic amines, have proved to be good electrophiles in Heck reactions with ethylene.[40] Attempts to introduce the vinyl moiety using organometallic species have also been described.[41] However, the use of vinyltrimethylsilane[41a] generally affords mixtures of styrene and trimethylsilylstyrene, while only one example has been reported concerning the use of vinyltrimethylstannane.[41b]

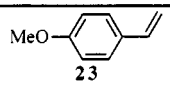
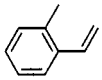
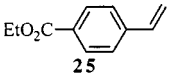
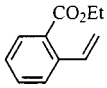
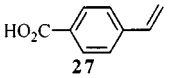
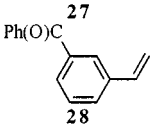
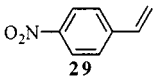
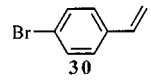
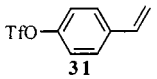
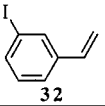
We were pleased to find that previously prepared potassium vinyltrifluoroborate **1j** is capable of acting as a highly efficient vinylating agent. Indeed, palladium-catalysed cross-coupling reactions of arenediazonium tetrafluoroborates with **1j** afforded styrene derivatives in good yields at room temperature (Table 5). The reaction was best performed using the palladacycle **8**[29] as catalyst and methanol as solvent.[42] It was found that use of a slight excess (1.2 equiv.) of the boron reagent led to improved yields of styrenes.

As indicated in Table 5, good yields of styrenes could be obtained even with catalyst ratios as low as 0.1% (entries 3, 4, 7, 8). Very fast initial rates were generally observed, with a reaction half-life of the order of 30 seconds. The nature of the substituents on the arenediazonium salt did not have a significant influence on the yield; substrates bearing both electron-withdrawing (ester, ketone, nitro) and electron-donating groups (methoxy, methyl) reacted smoothly with potassium vinyltrifluoroborate. Moreover, acidic groups, such as carboxy (entry 5) were tolerated in this coupling. Arenediazonium tetrafluoroborates bearing an *ortho* substituent also gave good yields of styrenes (entries 2 and 4).

Again, we examined the reactivity of the diazonium function relative to the halides and triflate by using arenediazonium tetrafluoroborates bearing iodide, bromide, or triflate substituents. In each case (entries 8−10), the diazonium functional group was clearly far more reactive and it was

Table 5. Formation of styrenes[a]

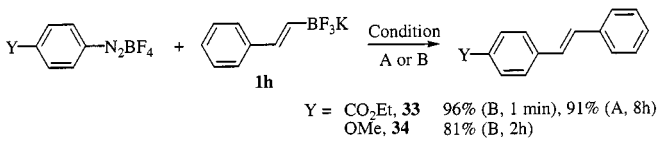


Entry	Catalyst **8** (%)	Time (min)	Styrene	Yield[b] (%)
1	1	20	 **23**	81
2	0.5	20	 **24**	78
3	0.1	120	 **25**	88
4	0.1	20	 **26**	70
5	1	15	 **27**	72
6	1	10	 **28**	81
7	0.1	15	 **29**	84
8	0.1	30	 **30**	69
9	0.5	60	 **31**	75
10	1	60	 **32**	76

[a] Reactions were conducted with 5 mmol of **2**, 1.2 equiv. of **1j** in the presence of a catalytic amount of **8**, in 10 ml of degassed methanol at 20°C. Conversions, determined by the volume of N_2 evolved, were quantitative. – [b] Yields of distilled products.

possible to obtain iodo-, bromo-, and (trifluoromethylsulfonyloxy)styrene in good yield.

This reaction was not limited to the simple potassium vinyltrifluoroborate **1j**. Thus, under the described conditions, cross-coupling of diazonium salts with potassium styryltrifluoroborate **1h** afforded stilbene derivatives in high yields (Scheme 8). Once again, conditions B permitted shorter reaction times and led to higher yields. Indeed, the coupling with **2b** was instantaneous at room temperature and subsequent simple filtration gave the pure product **33**.

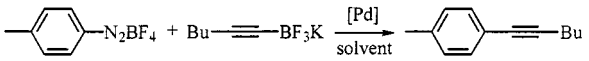


Scheme 8. Formation of stilbene derivatives

Cross-Coupling Reactions with Potassium Alkynyltrifluoroborates

Finally, we attempted to extend the above coupling to the formation of sp^2–sp carbon–carbon bonds using potassium alkynyltrifluoroborates. The reaction was studied on a model system, the coupling of **2a** with **1n** (Table 6).

Table 6. Cross-coupling reactions with potassium alkynyltrifluoroborates[a]



2a **1n** **35**

Entry	Catalyst	Solvent	Time (h)	Conv[b]	Composition of the mixture[c] (%) **35**	**4**	**6**	Bu≡≡Bu
1	**8**	MeOH	10	80	2	88	5	< 1
2	$Pd(OAc)_2$	dioxane	12	90	4	96	0	5
3	$Pd(acac)_2$	dioxane	8	70	9	91	0	2
4	$Pd(dba)_2$	dioxane	< 24	80	15	85	traces	6
5	**8**	dioxane	2	75	traces	100	0	traces

[a] Reactions were conducted with 1 mmol of **2a**, 1.2 equiv. of **1n** with 5 mol% of catalyst, in 4 ml of solvent at room temperature. – [b] Conversions determined by the volume of N_2 evolved. – [c] Determined by GC/MS.

Using the proven catalytic systems described above, i.e. **8**/methanol (entry 1) and $Pd(OAc)_2$/dioxane (entry 2), we observed only small amounts of **35** in the crude reaction mixtures and the diazonium salt **2a** was quantitatively reduced. Likewise, the use of other palladium complexes in dioxane did not lead to good yields of alkyne **35**. Toluene **4** was invariably found as the major product. Moreover, conversions remained below 100% and the catalyst seemed to decompose very rapidly.

When **2a** was treated with **1n** in 1,4-dioxane at 20°C in the absence of any palladium catalyst, a red coloration appeared, which intensified with time. After several hours, GC analysis of the crude reaction mixture revealed the formation of numerous products, the major one being **4**. The red coloration may have been due to the formation of charge-transfer complexes,[43] with potassium alkynyltrifluoroborate **1n** acting as the electron donor. A monoelectronic exchange within this complex could have resulted in homolytic decomposition of the two substrates, thereby accounting for the formation of various compounds. Such a phenomenon has been observed previously in oxidative cross-coupling reactions of arenediazonium salts with organostannanes.[44]

Conclusion

We have shown that potassium aryl- and alkenyltrifluoroborates may be efficiently employed as organometallic partners in palladium-catalysed cross-coupling reactions with arenediazonium salts. These reagents have been found to be more reactive than the corresponding organoboronic acids in such couplings.[45] Moreover, their ready availability, high stability, and ease of purification makes them eminently suitable for such applications.

Starting from inexpensive aromatic amines, it has proved possible to gain very efficient access to biaryl and styrene derivatives. The mild conditions (room temperature, absence of any bases or additives) and the very rapid reactions, achieved even at low catalytic ratios, makes this coupling one of the most efficient yet reported.

Moreover, this cross-coupling reaction has been shown to be chemoselective as it was possible to selectively couple the diazonium group in the presence of triflate, bromo, and, in many cases, iodo substituents. This high reactivity of the diazonium group suggests the possibility of iterative cross-coupling reactions.

Experimental Section

General: ^{1}H-NMR spectra were recorded on Bruker AC 200, AM 250, or ARX 400 spectrometers at 200, 250, and 400 MHz, respectively; chemical shifts (δ) are reported in ppm, referenced to Me_4Si; coupling constants (*J*) are reported in Hertz and refer to apparent peak multiplicities. ^{13}C-NMR spectra were recorded on the same Bruker AC 200, AM 250, or ARX 400 instruments at 50, 63, or 200 MHz. ^{11}B- and ^{19}F-NMR spectra were recorded on a Bruker AM 250 instrument at 80 and 233 MHz, respectively, using $BF_3{\cdot}Et_2O$ as an internal reference. − Mass spectra were recorded on a Ribermag instrument. − Elemental analyses were performed at the Regional Microanalysis Service (Université Pierre et Marie Curie). − Thin-layer chromatography was carried out on silica gel plates (Merck F_{254}) and spots were visualized under UV light.

1,4-Dioxane (from SDS) was distilled over $LiAlH_4$; it was stored over 4-Å molecular sieves and carefully degassed prior to use. Anhydrous THF and diethyl ether were distilled over sodium/benzophenone, while CH_2Cl_2 was distilled over calcium hydride. $Pd(OAc)_2$ and aromatic amines were purchased from Acros or Aldrich and were used as received, except in the case of aminophenols, which were recrystallized from ethanol. Arylboronic acids were obtained from Lancaster Synthesis, Acros, or Fluka, trifluoromethanesulfonyl chloride from Fluka. Commercial trialkyloxyboranes were distilled over sodium prior to use. Alkenylboronic acids were prepared according to literature procedures.[46]

General Procedure for the Formation of Potassium Organotrifluoroborates from Organoboronic Acids and Esters: To a concentrated solution of the organoboronic acid or ester in methanol at room temperature, a saturated aqueous solution of KHF_2 (3.3 equiv.; CAUTION: use a Teflon vessel) was added dropwise. A heavy white precipitate was deposited. Following the addition, the solvent was removed in vacuo at 40−50°C and the residual solid was thoroughly dried. It was then extracted with acetone (twice at room temperature and twice with boiling solvent), the combined extracts were filtered, and the solvent was evaporated. The powder obtained was redissolved in the minimum volume of boiling acetone, the solution was filtered, and then allowed to cool to room temperature, whereupon the salt precipitated. Precipitation was completed by the addition of diethyl ether. The white solid was filtered off, washed thoroughly with diethyl ether, and dried in vacuo. In the ^{13}C-NMR spectrum, the signal of the carbon in the position to the tetravalent boron was generally not observed.

Potassium Vinyltrifluoroborate 1j from Vinylmagnesium Chloride: To a solution of trimethoxyborane (34 mL, 0.3 mol) in anhydrous THF (200 mL), a 15% solution of vinylmagnesium chloride in THF (120 mL, 0.2 mol) was added dropwise, with the internal temperature being maintained below −60°C. The mixture was mechanically stirred under argon for 30 min. at −60°C, allowed to warm to room temperature, and then stirred for a further 30 min. Potassium hydrogen difluoride (94 g, 1.2 mol) was added in a single portion at 0°C, and then water (200 mL) was slowly added, which resulted in the deposition of a voluminous white precipitate. The resulting suspension was stirred for 30 min at room temperature and then the solvents were removed in vacuo (bath temperature 50°C). After treatment as described in the general procedure (extraction, precipitation), 22.53 g (84% yield) of potassium vinyltrifluoroborate **1j** was obtained as a white solid; m.p. 241°C (acetone/diethyl ether), ref.[16a] 225°C (dec.). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.1−5.4 (br m, 2 H, 2-H), 5.86 (ddq, J_{HH} = 19.8 and 14.4 Hz, J_{HB} = 3.8 Hz, 1 H, 1-H). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 121.1 (q, J_{CB} = 4.7 Hz, C-2). − ^{11}B NMR (80 MHz, [D$_6$]acetone): δ = 3.4 (q, *J* = 56 Hz). − ^{19}F NMR (235 MHz, [D$_6$]acetone): δ = 7.1 (q, *J* = 54 Hz). − $C_2H_3BF_3K$ (133.95): calcd. C 17.93, H 2.26; found C 17.78, H 2.35.

In situ Formation of Potassium Aryltrifluoroborates from Aryl Bromides: Preparation of Potassium (4-Methoxyphenyl)trifluoroborate (1k): To a solution of 4-bromoanisole (5.61 g, 30 mmol) in anhydrous diethyl ether (30 mL), a solution of *s*-BuLi (0.85 M in hexanes, 35 mL, 30 mmol) was added dropwise, with the internal temperature being maintained below −75°C. The mixture was mechanically stirred for 1 h at this temperature and then for 30 min at room temperature. It was then cooled to −78°C and cannulated into a solution of triisopropyloxyborane (6.8 mL, 36 mmol) in diethyl ether (100 mL), with the temperature being kept below −75°C. The resulting mixture was stirred for 1 h at this temperature and then for 30 min. at room temperature. A saturated aqueous solution of KHF_2 (9.4 g, 120 mmol) was then added dropwise and the solvent was removed in vacuo. After treatment as described in the general procedure (extraction, precipitation), 5.46 g (85% yield) of **1k** was obtained as a white solid; m.p. > 260°C (acetone/diethyl ether). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 3.70 (s, 3 H, OCH_3), 6.68 (d, *J* = 8.5 Hz, 2 H, 3-H), 7.38 (d, *J* = 8.5 Hz, 2 H, 2-H). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 54.9 (s, OCH_3), 112.6 (s, C-3), 133.4 (s, C-2), 158.2 (s, C-4). − ^{11}B NMR (80 MHz, [D$_6$]acetone): δ = 4.4 (br q, *J* = 53 Hz). − ^{19}F NMR (235 MHz, [D$_6$]acetone): δ = 8.0 (br q, *J* = 50 Hz). − $C_7H_7BF_3KO$ (214.03): calcd. C 39.28, H 3.30; found C 39.30, H 3.39.

General Procedure for the in situ Formation of Potassium Alkenyltrifluoroborates: Preparation of Potassium (*Z*)-(1,4-Dichlorobut-2-en-2-yl)trifluoroborate (1m): To a solution of (−)-α-pinene (17.9 mL, 115 mmol) in anhydrous THF (50 mL) at 0°C, $BH_3 \cdot Me_2S$ (5 mL, 50 mmol) was added over a period of 10−15 min. The resulting mixture was stirred for 1 h at 0°C and then for 2 h at room temperature. At −40°C, this colourless solution was treated with a solution of 1,4-dichlorobut-2-yne (4.89 mL, 50 mmol) in THF (50 mL). The mixture was stirred for 1 h at −40°C and was then left to stand at room temperature for 5 h. Acetaldehyde (40 mL, 14 equiv.) was subsequently added at 0°C, the solution was heated to 35°C for 15 h, and transferred via a cannula into a saturated aqueous solution of KHF_2 (15.6 g, 0.2 mol) at 0°C. Following the addition, the mixture was stirred for 15 min at room temperature and then the solvent was removed in vacuo (bath temperature 40−50°C). The dry solid residue was extracted with acetone (3× 50 mL), the combined extracts were filtered, and the solvent was evaporated. The resulting powder was redissolved in the minimum volume of acetone, and then diethyl ether was added to precipitate the organotrifluoroborate. The suspension was stored overnight at −20°C to complete the precipitation. The white precipitate was filtered off, washed thoroughly with diethyl ether, and dried in vacuo to afford 5.16 g of **1m** (45% yield) as a white solid; m.p.

180−185°C (dec.) (acetone/diethyl ether). The compound was stored at 0°C. − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 4.16 (s, 2 H, 1-CH$_2$), 4.23 (dd, J = 7.6 and 0.7 Hz, 2 H, 4-CH$_2$), 5.87 (t, J = 7.6 Hz, 1 H, 3-CH). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 41.3 (s, C-1 and C-4), 131.1 (q, J_{CB} = 2.8 Hz, C-3). − ^{11}B NMR (80 MHz, [D$_6$]acetone): δ = 3.0 (q, J = 51 Hz). − $C_4H_5BCl_2F_3K$ (230.89): calcd. C 20.81, H 2.18; found C 21.21, H 2.46.

General Procedure for the Formation of Potassium Alkynyltrifluoroborates: Preparation of Potassium (Hex-1-yn-1-yl)trifluoroborate (1n): To a solution of hex-1-yne (2.3 mL, 20 mmol) in anhydrous THF (20 mL), a solution of *n*BuLi (2.27 M in hexanes, 8.8 mL, 20 mmol) was added dropwise, with the internal temperature being maintained below −50°C. The resulting yellow solution was stirred for a further 10 min. and then cannulated into a solution of trimethoxyborane (4.2 mL, 40 mmol) in anhydrous THF (25 mL) at −78°C. After stirring for 1 h at this temperature, the mixture was cooled to −20°C for 30 min. A saturated aqueous solution of KHF_2 (12.5 g, 8 equiv.) was then added dropwise, with the temperature being kept at 0−5°C. The solvent was subsequently removed in vacuo (bath temperature 40°C). After treatment as described in the general procedure (extraction, precipitation), 2.93 g of **1n** (78% yield) was obtained as a white solid; m.p. > 260°C (acetone/diethyl ether). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 0.85 (m, 3 H, 6-H), 1.27−1.37 (m, 4 H, 4-H and 5-H), 1.94−2.02 (m, 2 H, 3-H). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 13.8 (s, C-6), 18.8 (s, C-3), 21.7 (s, C-5), 31.3 (s, C-4), 89 (br m, C-2). − ^{11}B NMR (80 MHz, [D$_6$]acetone): δ = −1.78 (q, J = 38 Hz). − ^{19}F NMR (376 MHz, [D$_6$]acetone): δ = 17.7 (q, J = 37 Hz). − $C_6H_9BF_3K$ (188.03): calcd. C 38.33, H 4.82; found C 38.20, H 4.91.

Formation of Arenediazonium Tetrafluoroborates (2):[7a,7b] At 0−5°C, the appropriate aromatic amine was dissolved in the minimum volume of water containing 50% aqueous HBF_4 (2.5 equiv.). To this solution, a saturated aqueous solution of sodium nitrite (1.2 equiv.) was added dropwise. During the course of the addition, a voluminous precipitate was formed and hence vigorous stirring was required. The mixture was stirred for 30 min. at this temperature and then the solid was filtered off. It was washed with 5% aqueous HBF_4, cold (< 0°C) methanol (products soluble in methanol were washed with cold 4:1 methanol/diethyl ether), and thoroughly with diethyl ether. It was then dried in vacuo with protection from light. The salts were purified by precipitation or recrystallization from acetone/diethyl ether or methanol/diethyl ether (temperature not exceeding 35−40°C). It was found that the products could be stored under an inert atmosphere at −20°C for years without noticeable decomposition.

The following arenediazonium salts were prepared according to this procedure: **2a** [459−44−9], **2b** [19262−74−9], **2c** [456−27−9], **2f** [7438−18−8], **2g** [459−45−0], and 4-methoxybenzenediazonium tetrafluoroborate [459−64−3].

Water-soluble arenediazonium salts were more conveniently prepared under anhydrous conditions[7c] (e.g. 4-carboxybenzenediazonium tetrafluoroborate [456−25−7]).

2-(Trifluoromethanesulfonyloxy)benzenediazonium Tetrafluoroborate (2h): To a suspension of 2-aminophenol (0.546 g, 5 mmol) in anhydrous dichloromethane (20 mL) under argon atmosphere, triethylamine (0.695 mL, 5 mmol) was added at room temperature. The mixture was stirred for 30 min and then cooled to −50°C. A solution of trifluoromethanesulfonyl chloride (0.529 mL, 5 mmol) in anhydrous dichloromethane (3 mL) was then added over a period of 10 min, with the temperature being maintained at −50°C. The resulting orange mixture was stirred for 30 min at −50°C and then for 1 h at room temperature. Diethyl ether (50 mL) was added and the suspension was filtered. The filtrate was washed with brine (3× 10 mL), dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel gave 1.025 g (85% yield) of 2-(aminophenyl)trifluoromethanesulfonate as a light-brown oil. − R_f = 0.59 (CH_2Cl_2). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.94 (br s, 2 H, NH_2), 6.7−6.9 (m, 2 H), 7.16 (pseudo t, J = 7.5 Hz, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 117.5 (s, 1 C), 118.5 (q, J_{CF} = 318 Hz, CF_3), 118.7 (s, 1 C), 121.8 (s, 1 C), 129.0 (s, 1 C), 136.9 (s, 1 C), 138.8 (s, 1 C). Diazotization of this amine according to the procedure of Doyle et al.[7c] and subsequent purification by rapid precipitation from methanol/diethyl ether afforded 1.367 g (90% yield) of **2h** as a white solid; m.p. 174−176°C (dec.) (methanol/diethyl ether). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 8.16 (ddd, J = 8.3, 7.8 and 1.0 Hz, 1 H, 5-H), 8.26 (dd, J = 8.7 and 1.0 Hz, 1 H, 3-H), 8.63 (ddd, J = 8.7, 7.8 and 1.6 Hz, 1 H, 4-H), 9.07 (dd, J = 8.3 and 1.6 Hz, 1 H, 6-H). − ^{13}C NMR (63 MHz, [D$_6$]acetone): δ = 109.6 (s, C-1), 119.0 (q, J_{CF} = 320 Hz, CF_3), 123.5 (s, C-3), 131.1 (s, C-5), 136.1 (s, C-6), 145.3 (s, C-4), 148.6 (s, C-2).

Cross-Coupling Reaction. − General Procedure: The arenediazonium tetrafluoroborate, the potassium organotrifluoroborate (1.2 equiv.), and 5 mol-% palladium catalyst were placed in a flask under argon atmosphere with protection from light (aluminium foil). Degassed solvent (4 mL/mmol) was added at 20°C and the mixture was stirred at this temperature until the evolution of N_2 had ceased (1 mmol, 24−25 cm^3). The reaction mixture was then diluted with diethyl ether and washed 3 times with brine. The organic phase was dried with magnesium sulfate, filtered, and the solvent was removed in vacuo. The crude product was generally purified by chromatography on silica gel (biaryls and some styrenes) or by kugelrohr distillation in the presence of 4-*tert*-butylcatechol (other styrenes).

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Received December 17, 1998
[O98568]